Electron Spin Resonance Spectra of Difluorodiazirine and Perfluoro Semidione Anion Radicals[1]

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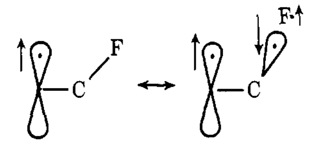
Abstract: The esr spectra of difluorodiazirine, perfluorobiacetyl, tetrafluorocyclobutane-1,2-dione, and hexafluorothioacetone radical anions are reported. INDO calculations for difluorodiazirine radical anion suggest that the fluorine hyperfine splitting is negative in sign and that spiroconjugation is less important than spin polarization mechanisms.

To date a limited number of small perfluoro radical anions have been reported and each is unique and all are surprisingly stable when contrasted with the hydrogen analog. We would like to report several new perfluoro radical anions, specifically those derived from perfluorobiacetyl, 1,2-perfluorocyclobutanedione, hexafluorothioacetone, and difluorodiazirine. Difluorodiazirine anion radical is particularly pertinent to the mechanism of fluorine coupling. The literature contains several discussions based on experimental data[2-13] or theoretical calculation[14-16] of hyperfine splitting by fluorine atoms attached to a carbon α to the radical center (β fluorine). Among the interactions considered have been p–σ overlap (1), 1,3 p_z–p_z overlap (2), 1,3 p_z–p_x overlap (3) and spin polarization through the single bonds.



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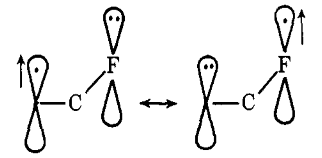

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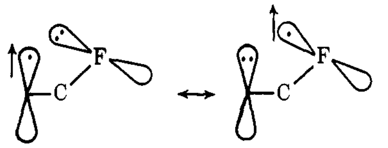

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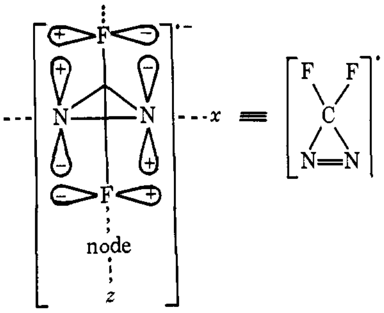
We thought that a unique system which would eliminate **1** and **2** from consideration would be the difluorodiazirine radical anion **4**. Because of the position of the node in ψ_2 for **4** (dotted line in structure), delocalization mechanisms 1 and 2 would predict $\rho_F = 0$ since $\rho_F = (c_{N_1} + c_{N_2})^2$.[17] As indicated in the structure, interaction 3 now results in spiroconjugation.[18,19] *Ab initio* calculations support this concept.[20] The π^* SCF-MO computed for the ground-state geometry indicates a high spin density for the nitrogen p_x orbitals (z perpendicular to the plane of the ring system) and a small positive spin in the fluorine p_x orbitals.



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Electrolytic reduction of difluorodiazirine[21] in either THF, DMF, or CH_3CN afforded an intense signal (Figure 1a) which can be completely resolved upon addition of approximately 5% water (Figure 1b).[22,23] The completely resolved spectrum consists of a major 1:2:1 triplet split into 1:2:3:2:1 pentets. It seems unlikely that such a spectrum would be expected from the isomeric species $[F_2C{=}N{=}N]\cdot^-$. Hyperfine split-

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[22] Reduction with Li, Na, or K failed to yield a paramagnetic species. See also ref 10.

[23] A strong signal from $CF_3NO_2\cdot^-$ was observed if electrolysis was conducted in the presence of oxygen; however, this result was not reproducible and awaits further investigation.

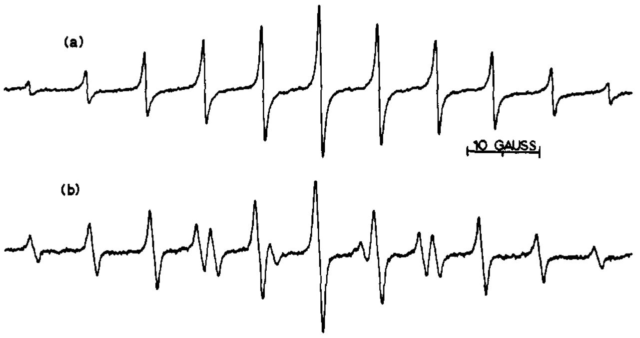


Figure 1. Difluorodiazirine radical anion (a) in dry tetrahydrofuran, $(C_2H_5)_4N^+$ gegenion; (b) in the presence of 5 vol % of water.

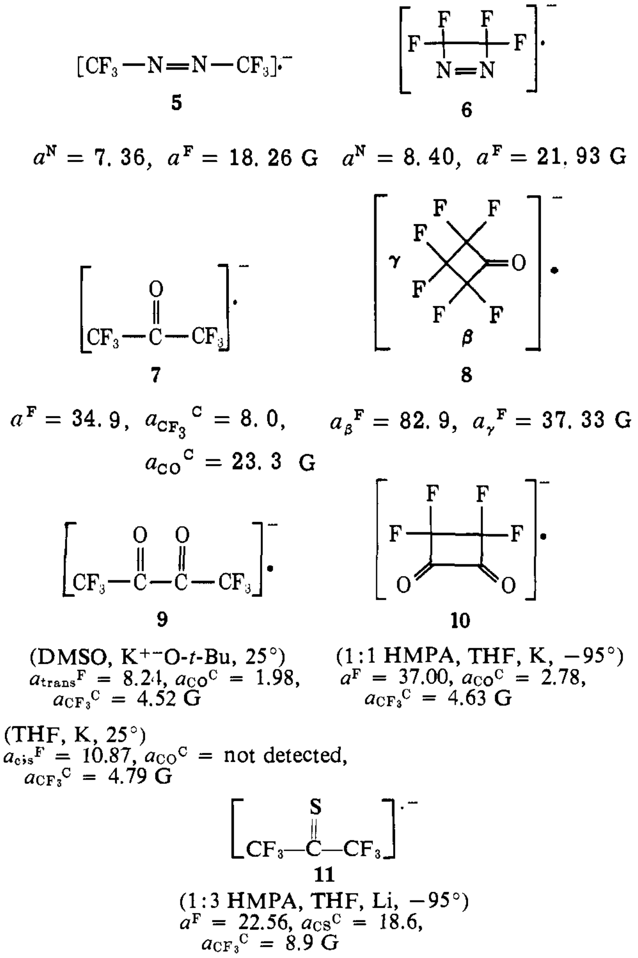
Table I. Difluorcdiazirine Radical Anion Hyperfine Splitting Constants in Gauss (25°)

Solvent	THF	THF[a]	DMF	DMF[a]	CH_3CN
a^N	8.05	8.16	7.98	8.13	8.05
a^F	24.05	22.65	24.48	23.39	24.07
a^C			5.65		

[a] Approximate 5% by volume water added.

ting constants (hfsc) are given in Table I and can be compared with other perfluoroazoalkane radical anions **5** and **6**,[10] and the ketyls **7**[9,24] and **8**.[8] We also report the hfsc for the perfluoro semidiones **9** and **10** and perfluorothioacetone, **11** (Scheme I).

Scheme I



$[CF_3{-}N{=}N{-}CF_3]^{\cdot-}$

$a^N = 7.36$, $a^F = 18.26$ G (**5**) $a^N = 8.40$, $a^F = 21.93$ G (**6**)

$a^F = 34.9$, $a_{CF_3}{}^C = 8.0$, $a_{CO}{}^C = 23.3$ G (**7**) $a_\beta{}^F = 82.9$, $a_\gamma{}^F = 37.33$ G (**8**)

(DMSO, $K^{+-}O$-*t*-Bu, 25°)
$a_{trans}{}^F = 8.24$, $a_{CO}{}^C = 1.98$,
$a_{CF_3}{}^C = 4.52$ G

(1:1 HMPA, THF, K, −95°)
$a^F = 37.00$, $a_{CO}{}^C = 2.78$,
$a_{CF_3}{}^C = 4.63$ G

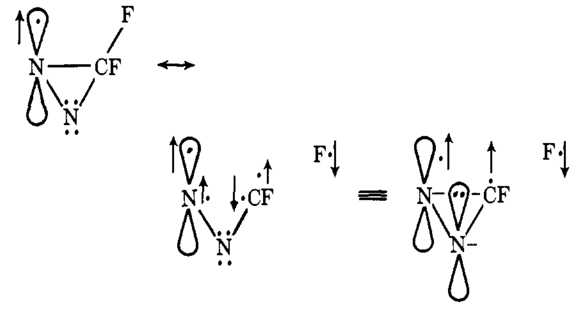
(THF, K, 25°)
$a_{cis}{}^F = 10.87$, $a_{CO}{}^C$ = not detected,
$a_{CF_3}{}^C = 4.79$ G

(1:3 HMPA, THF, Li, −95°)
$a^F = 22.56$, $a_{CS}{}^C = 18.6$,
$a_{CF_3}{}^C = 8.9$ G

The magnitude of a^F observed for **4** *appears* to support the idea of spiroconjugation. However the sign of a^F has not been measured.[25] Any delocalization mechanism (such as (3)) will require a positive sign for this hfsc. We investigated this by means of SCF calculations using the INDO approximation.[26] The potential energy minimum for the radical anion was calculated to have the following geometry: N=N = 1.33 Å, C-N = 1.39 Å, C-F = 1.37 Å, ∠FCF = 109.5°, and ∠NCN = 57.0°.[27,28] Using this geometry it was calculated that the singly occupied π MO is a combination of only the nitrogen p_z and fluorine p_z orbitals, *i.e.*, **4** as predicted.[20] However, because of spin polarization there exists spin density in other MO's. When the spin densities in all the MO's are summed, a negative spin density is obtained in all the fluorine orbitals with the fluorine 2s orbital having $\rho_{2s} = -0.0025$. Coupling constants were obtained from ρ_{2s} using the scaling factors of Pople, Beveridge, and Dobosh, *viz.*, C = 820, N = 379, F = 44,829 G (Table II). A value of 17,000 G is more consistent for the fluorine atom itself and would lead to a value of a^F in **4** of ~ -43 G. The predicted negative value of a^F in **4** would require a spin polarization mechanism, perhaps mechanism 5, wherein the spin induced would be proportional to $\rho_{N_1} + \rho_{N_2}$ (*i.e.*, $c_{N_1}{}^2 + c_{N_2}{}^2$).

Table II. INDO Calculated Hyperfine Splitting Constants for Difluorodiazirine Radical Ion

	a^F	a^N	a^C
Radical cation	+65.7	+9.4	−5.7
Radical anion	−112.8	+6.1	−4.4



(5)

Interestingly, the INDO calculation for the difluorodiazirine radical cation gave a positive value for a^F (Table II). Here the fluorine atoms are not in the nodel plane of the π system and delocalization mechanisms 1 and 2 apparently predominate over spin polarization.

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(28) Electron diffraction studies have given the vapor-phase geometry of N=N = 1.293 Å, C-N = 1.426 Å, C-F = 1.315 Å, ∠FCF = 111.84°, and ∠NCN = 53.95°: J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 5527 (1967).

Experimental Section

Perfluorobiacetyl,[29] 1,2-perfluorocyclobutanedione,[30] and hexafluorothioacetone[31] were prepared according to the literature. We wish to thank Dr. England for a generous gift of 1,2-dimethoxyhexafluorocyclobutane, the precursor of the dione.

Electrolytic reductions were performed in a vacuum electrolysis cell directly in the cavity of a Varian 4502 epr spectrometer. The electrolysis cell, Figure 2, consisted of (a) a platinum cathode in a flat fused silica cell, (b) a platinum anode isolated by a course glass frit, and (c) a freeze–thaw degassing chamber. The cell is conveniently prepared from fused silica microscope slides 1-mm thick. Samples to be reduced were transferred to the degassing chamber after the solvent and electrolyte (tetra-*n*-butylammonium perchlorate) have been freeze–thaw degassed under high vacuum for a minimum of four cycles. All solvents were distilled from calcium hydride prior to use. Tetrahydrofuran was stored over sodium benzophenone ketyl and distilled directly into the cell. Reduction of difluorodiazirine was performed at a potential drop of $\sim$2 V in DMF and CH$_3$CN and of $\sim$7 V in THF.

Many perfluoro substrates fail to yield detectable paramagnetic species when subjected to standard "alkali metal mirror" reduction, even at reduced temperature, although reduction is apparent.[7,8,10] We found that we could produce high concentrations (^{13}C hyperfine splitting easily detected) of such radicals if the substrate is reduced at low temperature ($\approx -100°$) by a solution of alkali metal in hexamethylphosphoramide (HMPA)–THF solvent mixtures. The following procedure was followed: (a) HMPA and alkali metal were freeze–thaw degassed under high vacuum in a cell designed for esr observation until a deep blue solution was produced (strong esr signal from solvated electron), (b) THF was then distilled into the cell from a sodium benzophenone ketyl solution, (c) the cell was sealed under vacuum and warmed to room temperature, (d) the deep blue solution was then used to "wash" the cell thereby removing traces of oxygen and moisture, and (e) the cell was cooled to $-100°$ and substrate added *via* break seal and immediately placed in the spectrometer (cavity at $-100°$) for observation. A moderate signal from solvated electron generally remained and slowly faded.

Perfluorobiacetyl semidione is easily generated at room temperature by a variety of reduction techniques.[32] Intense, sharp, well-resolved spectra are observed if reduction is performed *via* the HMPA–THF–alkali metal method (^{17}O in natural abundance detected).

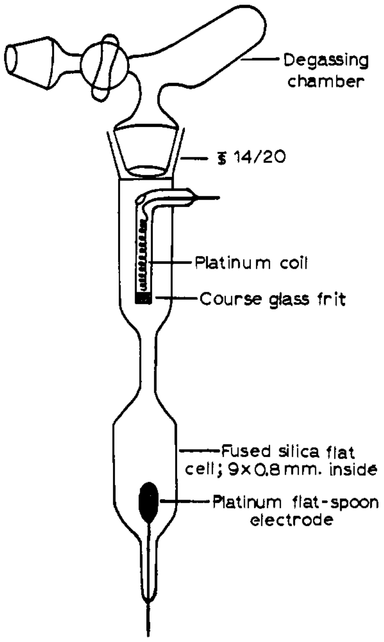

Figure 2. Apparatus for electrolytic reduction of volatile substrates. The electrolytic cell can be easily cooled to $-60°$ by a stream of cold nitrogen passing through an outer jacket inside the esr cavity.

We were unable to generate 1,2-perfluorocyclobutanedione semidione either by electrolysis (CH$_3$CN, DMF) or alkali metal mirror reduction in THF. A reasonable spectrum can be obtained if electrolysis is conducted in dry THF,[32] but an intense signal is obtained if the HMPA–THF–alkali metal method is employed. The spectrum of the semidione shows second-order splitting from four equivalent fluorine atoms, *i.e.*, a 1, 1:3, 1:3:2, 1:3, 1 pattern. The semidione decomposes rapidly as the temperature is raised above $\approx -40°$.

Hexafluorothioacetone is extremely sensitive to base catalyzed disulfide formation.[31] The material looses its blue color immediately when dissolved in dry CH$_3$CN, DMF, or THF and no paramagnetic species could be detected upon electrolysis or alkali metal reduction in these solvents. An intense spectrum can be observed if the HMPA–THF–alkali metal method is used. Apparently the rate of thioketyl production at $-100°$ greatly exceeds other reactions. The first-order signal fades rapidly above $\approx -80°$'

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